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The conductivity and nonlinear optical properties of small molecules beginning with the water molecule and further developed for hydrides and simple polymer molecules, including metal-ion containing polymers, are predicted based on ab initio techniques. These calculations are extended to the prediction, understanding, and improved design of polymer molecules for enhanced or controlled nonlinear properties. Specific predictions are provided for dipole polarizabilities and the first and second hyper-polarizabilities for small molecules.

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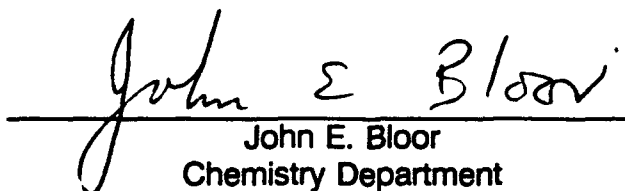
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MOLECULAR DYNAMICS CALCULATIONS OF OPTICAL NONLINEAR PROPERTIES OF MATERIALS

J. E. Bloor
Chemistry Department
The University of Tennessee
Knoxville, TN 37996-1600

Final Report For
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John E. Bloor
Chemistry Department

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Contract Title: Molecular Dynamics Calculations of Optical Nonlinear
                                Properties of Materials

Principal Investigator: John E. Bloor

NAVAIR Program Monitor: Dr. L. E. Sloter

Technical Objective: To develop theoretical methods for the prediction of new
                                materials with properties of interest to Naval Air Command

TECHNICAL ACCOMPLISHMENTS

A.   INTRODUCTION

In general, the research program has continued in the directions outlined in the original proposal except that, because of the departure of Dr. Y. G. Yu in February, six months earlier than expected, activity in the development of practical theoretical methods for the calculation of the conductivity and nonlinear optical properties of polymers was severely curtailed during the last six months of the project however two manuscripts have been written on this topic (Appendices II and III). However, considerable progress has been made in obtaining results from accurate calculations using ab initio methods (papers 1-3, Appendix I).

B.   TECHNICAL PROGRESS

1.   Ab Initio Calculations of Nonlinear Optical Properties for Small Molecules.

Although there are a large number of semi empirical calculations on nonlinear optical parameters available in the literature there have been until very recently very few accurate ab initio calculations of any kind on even diatomic molecules. Our philosophy is that, since the measurement of nonlinear optical properties per se is so difficult, the only way to put the semi empirical methods on a firm foundation is to provide accurate reference calculations on small molecules which can both be used to evaluate the results of semi empirical methods and also they can act as a guide in choosing parameters during the development of new semi empirical methods and in extending the present methods to the heavier elements. This task was regarded as one of the main aims of this research contract. Calculations on the following sets of molecules have been completed

and the results are in the process of being analyzed fully and written up for publication.

1.   Ab initio calculations on the water molecule Published. *Theochem.* <u>234</u>, 173-183

(1991)(Appendix 1, paper 3).

2.   Ab initio calculations on hydrogen cyanide and phosphaethyne (H-C≡P).

Published. *J. Phys. Chem.* <u>94</u>, 5586-5589 (1990)(Appendix 1, paper 2).

3.   Ab initio calculations on ammonia, formamide, pyrrole and pyridine. Manuscript

in preparation. (A preliminary version containing the results is attached, Appendix

II).

4.   Ab initio calculations on molecules of the type $H_2X = Y$ (X = C, Si, Ge; Y = O, S).

Manuscript in preparation.

5.   Ab initio calculations on phosphine and arsine (NH_3, PH_3). In preparation.

6.   Ab initio calculations on molecules of the type H_2X (X = S, Se, Te). In preparation.

7.   Ab initio calculations on molecules of the type XO_2 (X = S, Se, Te).   In

preparation.

8.   Ab initio calculations of model molecules containing silicon and germanium, e.g.,

of the type H-X≡X-H and X_2H_4. In preparation.

9.   Ab initio calculations of small molecules containing transition metals. Preliminary

results only. Work still in progress.

These calculations were designed primarily to give answers to the following

questions:

1.   How important are d and p polarization functions on the hydrogens?

2.   How important is the role of diffuse p functions on atoms other than hydrogen?

3. How small a basis set can we get away with without degrading the values of nonlinear parameters?

4. Can we approximate the core electrons by an effective potential without losing accuracy and thereby save CPU time and reduce memory requirements?

5. Are the basis sets found to be successful for small molecules transferable to larger molecules?

6. How important is electron correlation?

7. Are there any general rules which can be deduced form our experience which will help in future calculations?

8. How do the accurate results obtained compare with results of the semi empirical methods now in use?

Calculations on the hydrides of groups three, four, five and six fully confirm our prediction that there is a dramatic increase in the value of the second hyperpolarizability as we ascend a particular row of the periodic table. The calculations on compounds containing the heavier elements confirm our earlier results on extraordinary sensitivity of the β and γ values for the heavier elements to the presence of very diffuse basis functions on both the central atom and the hydrogens. For example in calculations on compounds of gallium, it was found that one extra set of diffuse p functions over those we thought would be adequate changed the value of $\bar{\gamma}$ by a factor of four.

The most difficult problem we have had to solve is the calculation of accurate values of all the first hyperpolarizabilities (β) in one calculation. Our results for the

hydrides (e.g., the paper 3 in Appendix I on the water molecule) show that the β values are very sensitive to the number and type of polarization functions placed on the hydrogens. In particular, it was found necessary for the heavier elements to have multiple sets of both p and d functions (very diffuse functions) present. Moreover, these functions seem to interact in a complicated way so that erratic values of certain β values are obtained by leaving off one or more functions. Also it was found that this sensitivity was different for different elements. For example, the calculation on the β parameters for selenium compounds require a different set of polarization functions on the hydrogen than for arsenic. Reliable values can be obtained by saturating the hydrogens with five sets each of d and p functions with exponents of 1.0, 0.5, 0.25, 0.125, 0.0625 but for a molecule like AsH_3 even at the Hartree-Fock level this becomes prohibitive in terms of computer time and disk space. Moreover, with multiple sets of polarization functions converge problems occur. These problems make it impossible to perform this type of calculation on a main frame computer which is used by others, since the calculations are I/O bond, and have to reside in the computer for more than seven days, which means they are often lost due to system crashes or the taking over of the computer by the sytsem programmers for maintenance and updating. We have overcome this difficulty to some extent by purchasing a IBM RISC/6000 work station and dedicating it for long periods of time to the calculation of nonlinear optical properties. However our limited budget prevented us from purchasing an external disk drive larger than 1.2 gigabytes so we are somewhat restricted in the size of the basis set we can employ (<200 basis functions). However, despite these problems, we were able to obtain fairly accurate

values for the molecules listed above. This is a tremendous advance over the values in the literature which are restricted to formaldehyde (CH_2O), water (H_2O), ammonia (NH_3) and few diatomics and most of these have appeared in the last year or so.

If we can be satisfied with less accurate β values (say with errors of 30%-50% for may be one matrix element with the others within 20%) then we have found that reliable values of the dipole polarizabilities (α) and hyperpolarizabilties (γ) can be obtained fairly easily for molecules containing more than a dozen atoms. This is exemplified by our calculations on pyridine and pyrrole in the manuscript in Appendix II. We are now pursuing this approach vigorously for molecules containing the heavier elements. The problem here is that we need realistic geometries. However, we believe we have solved this problem as described later in this report.

Anotehr aspect of our work, which we have been the first to investigate systematically, is the role of electron correlation. Sadlej (e.g., *Theoretica Chimica Acta* 79, 123-160 (1991)) demonstrated the importance of including electron correlation for dipole polarizabilities. His group has been using many body perturbation theory (MBPT) to fourth order. We have applied Moller-Plesser perturbation theory to second order (MP2) and have obtained very similar results except that we have also got data, for the first time, for the effect of including electron correlation for the first hyperpolarizabilties (β) and we have started work on the second hyperpolarizabilties (γ). The results for β show that the effect of including correlation is much greater for these parameters than it is for the α values.

Indeed, one of our main conclusions is that it is a very difficult and time consuming

task to get accurate values for even the smallest molecule. However it is possible to get approximate values and this should be pursued in preference to rushing ahead to get values, which are, probably meaningless, from a semi empirical method which has been inadequately tested out on smaller molecules.

Since we consider the production of accurate values of nonlinear optical parameters of reference molecules to be a necessary requirement before the development of semi empirical methods, our attention in the latter half of 1991 was focused on whether reliable ab initio values of nonlinear optical parameters could be attained using smaller basis sets than we found necessary for very accurate calculations. One method we have explored is to describe the behavior of the inner electrons by an effective core potential (ECP method). Progress in this area is described in the next section.

2.   Effective Core Potential Calculations

There are many reports in the literature on methods for the development of effective core potentials (ECPs) as a substitute for the explicit treatment of the inner electrons (i.e., those with a different (lower) principal quantum number than that of the valence electrons) which are thought to be responsible for the major part of the binding in a molecule. However, there have been relatively few attempts to actually use the ECP method   for the calculation of molecular properties, other than the energy. Since our interest is in the calculation of electric field effects and these are sensitive primarily to the outermost electronic density it seemed reasonable to try out the use of ECPs for the purpose of carrying out calculations of nonlinear optical parameters.

Although the study is still in its infancy enough results have been obtained to indicate that this is a viable way to proceed, especially for molecules containing heavier elements, since the saving in computer time and disk space becomes relatively greater the greater the ratio of the number of core electrons to valence electrons becomes. At the same time as we have investigated the use of an ECP we have also attempted the dangerous, but nevertheless necessary, procedure of reducing the number of diffuse functions used in the calculations of larger molecules, by using our experience with the accurate calculations to choose only those functions found to be most sensitive to the applied field. The results given in Appendix II for formamide ($HCONH_2$) are typical of the results obtained. Formamide was chosen because a) it is a very polar molecule with a large amount of charge transfer between a donor (NH_2) group and an acceptor ($C = O$) group which should, if qualitative ideas on the relationship between structure and large hyperpolarizabilities have any validity, result in enhanced γ and β values compared to the values of the parent molecules (ammonia, formaldehyde); b) there are previous semi empirical calculations; and c) there is considerable interest in having α, β, and γ values for this molecules as a prototype building block for polypeptides. These results show that using the ECP method results in a considerable saving in computer time with little change in the numerical accuracy of the results. Similar results have been obtained for larger nitrogen compounds (e.g., pyrrole and pyridine)(see Appendix II).

3.   Beyond the Hartree-Fock Zero Frequency Static Field Methodology

Before one can expect a good one to one relationship between experiment and theory for nonlinear optical parameters, one must have calculations which, in addition to

an adequate basis set, must also include electron correlation and also which include the dynamic frequency dependence. Our computer codes have been modified to include both these effects although, at the moment, calculations on the effect of electron correlation on the second hyperpolarizability have to be obtained by performing a number of separate calculations containing electric fields of varying strength at a number of different positions and then using the appropriate expansion formulae, a very laborious process. Typical of the results obtained are those we obtained for *formamide* (Appendix II, Table 2) for including electron correlation at the MP2 level. While expecting an increase in computer time we were somewhat unprepared for the large increase experienced even for *an* atom. It was also found that it was necessary to increase the convergence criterion on the total energy by one or two orders of magnitude to get numerically accurate values of the first polarizability. (This finding leads us to question on the grounds of numerical accuracy alone many literature β values obtained using semi empirical methods, since these usually employ higher tolerances for energy convergence than we have found to be necessary. The values obtained in these calculations, and others, show that including the electron correlation changes the hyperpolarizabilities by a factor between 1.5 and 2.0.

4.   Geometry Determination

In calculations on the more common molecules, such as formamide or pyridine, experimental geometries are available and can be used, but for the more exotic molecules containing tellurium or arsenic experimental geometry studies are relatively rare. In principle one can perform theoretical geometry optimizations using either ab initio or semi

empirical techniques.   However, semi empirical techniques for molecules containing heavier atoms are notoriously unreliable. Also there have been few ab initio studies on molecules containing more than five or six atoms and on molecules containing atoms of the third and higher periods (e.g., our study on the geometry of SO_2 (Appendix I, paper 1). Moreover, there have been very few attempts to use ECP gradient methods to obtain geometries. For these reasons we have been looking at methods for the calculation of geometries.   As soon as we find more that 6-10 atoms in a molecule we ran into computational problems. This was traced to a lack of stability in the initial Hassian matrix used to calculate the force constants needed to start the geometry optimizations especially for cyclic molecules. A new method was developed and implemented by Dr. Yu. This required an initial semi empirical (AM1 method) geometry optimization, followed by a force constant calculation. The force constants were then used as the starting point for the ab initio calculation. Even though the calculated semi empirical geometry could be poor the force constants calculated using it were found to facilitate the convergence of the ab initio geometry optimization considerably and cut down the computer time required by one or two orders of magnitude. This has enabled us to perform geometry optimizations on relatively large molecules and as benzothiophen C_8H_6S. Examples of applications of this procedure are being written up separately from the nonlinear optical parameter studies, but an adequate geometry optimization method is a necessary prerequisite before the hyperpolarizability calculations are even begun.

Another problem we encountered in the geometry calculations was the problem of what basis set to use.   Even though the basis set requirement of geometry

optimizations is nowhere near the stringent requirements of the nonlinear optical parameter calculations, some polarization functions are needed. There have however been few studies made on how to choose these functions. We have therefore extended our study on the SO_2 molecule to study molecules of the general type MO_n where M is S, Se, Te, Cr and Mo and n is 1, 2 or 3. As a check on the calculations we have also performed vibration frequency calculations since matrix isolation experiments of these quantities are often more available for "exotic" molecules than are geometry studies. These results have been generally good (e.g., TeO_2) however the results on the geometry of SeO_3 have been uniformly poor. In every calculation we have tried, including a very extensive configuration interaction calculation, the bond distance has always been much shorter than experiment even though the vibration frequencies have been reasonable. This has lead us to suspect the experimental values rather than the theoretical methods so we are proceeding to other molecules, leaving this molecule alone until more experience has been obtained on the type of basis set we have to employ to get reasonable geometries. Calculations on other small molecules containing transition metal atoms are either completed and awaiting analysis or are in progress.

5.   Ab initio calculation of Polymers

The other main thrust of the research program was to develop a computer code for the calculation of the electronic structure of organic polymers. The method chosen was one developed over the last two decades by the research group of Professor J. J. Ladik at the Friederich Alexander University at Erlangen - Nürnberg, Germany. This program has been used previously to investigate vibrational and transport properties of

organic polymers and is the only program which incorporates electron correlation into its formalism. We have installed this program at the University of Tennessee and Professor J. Ladik visited us for a period during November and December (1989) to instruct us in matters concerning the use of the program. We have used this program to calculate band structures of polymers containing elements from the third and higher groups of the periodic table. As might be expected, for a problem of this complexity, the calculations are not easy to perform and it is very easy to get false results. The program for example is very sensitive to the geometry and is very difficult to get converged results with the larger basis sets we would like to use! In addition to the problem of basis set size we also have the problem of how many interacting neighbors are to be included. Typical of the results we have been able to complete is a study of the electronic band structure of polyethylene, polysilene and polygermane using two basis sets, i.e., a minimal basis and a double zeta set. A manuscript describing this work is in preparation (see Appendices III and IV). The main feature of the work is that it demonstrates the dramatic drop in band gap in going from the carbon polymer (24.0, 15.6 eV) to the silicon polymer (14.1, 10.2 eV) and the germanium polymer (9.3 eV,*). (The minimum basis result is given first, the double zeta value second.) (* means that for the Ge polymer indicates we were not able to get convergence after many tries!) These values cannot be compared with experiment quantitatively because we do not yet have correlation effects in our method. However the trend should be qualitatively correct. Analysis of the orbitals involved in the band gap show that although Sc and Ge behave similarly they are considerably different from carbon. The results support the idea that in these molecules there is considerable

delocalization of the sigma electrons.

6. The Calculation of Nonlinear Properties of Polymers

No one has yet succeeded in developing a <u>working</u> method for the calculation of the nonlinear optical properties of polymers. Ladik recently suggested a formalism for doing these calculations and since we already had the necessary polymer code the extension of the method in this direction was a reasonable project to attempt. This was a very formidable task but was completed by the end of the summer (1990) by my colleague, Dr. J. G. Yu. Since then calculations have been completed and compared with calculations on small similar molecules calculated by the Hartree Fock methods described in Appendix III. The basic difficulty in the methods proposed for calculating electric field effects of polymers is that because of the term $|e|$ E_zZ (E_z being the electric field in the z direction) the chain will become non-periodic. In order to get around this difficulty Ladik suggested that the polymer chain of $2N_A + 1$ unit cells be divided into $2N_B + 1$ segments ($N_B < N_A$). Each segment is then allowed to contain a certain number of unit cells each of which are given an average value for the dipole moment component $\bar{Z}_M$. The success of the method then depends upon the insensitivity of the parameter to the way the partitioning was made. Our initial calculations on polyethylene and its silicon and germanium analogues using a minimal basis set were quite successful (Appendix III) but we are running into problems when we increase the size of the basis set and at the present time we have not come up with a satisfactory scaling method which is completely independent of basis set.

The computer code has been extended to calculate the second hyperpolarizabilities

(γ) and has also been written and tried out using minimal basis sets purely as a means of checking the numerical accuracy. As expected for such a small basis set the results are physically meaningless so they are not quoted here.

CO-INVESTIGATORS

1. Professor Jianguo Yu (Bejing, China). Post-doctoral fellow, University of Tennessee, June 1, 1989 — February 1990.

2. Professor J. Ladik, director of the Physical Chemistry Institute, Friederich Alexander University, Erlanger, Nürnberg, Germany. Visiting Professor at University of Tennessee, October 1 - November 30, 1989.

3. P. C. Yih. Part time Graduate Assistant, June 1991 — present.

PUBLICATIONS

1. J. Bloor, "Ab Initio Calculations of Harmonic Vibrational Frequencies and Intensities of Molecules Containing Atoms of the Third Period of the Periodic Table. I. Hydrogen Sulfide and Sulfur Dioxide," *International Journal of Quantum Chemistry*, Symposium 23, 187-197 (1989).

2. J. E. Bloor and J. Yu, "Ab Initio Prediction of the Geometry, Vibration Properties, Polarizabilities and First Hyperpolarizabilities of Phosphaethyne," *J. Phys. Chem.*, 94, 5586-5589 (1990).

3. J. Yu, S. Su, and J. E. Bloor, "Ab Initio Calculations on the Geometries and Stabilities of Acetylene Complexes," *J. Phys. Chem.*, 5589-5592 (1990).

4. J. E. Bloor, "Finite Field Ab Initio Calculations of the Dipole Polarizabilities and First and Second Hyperpolarizabilities Using Multiple Sets of Polarization Functions I.

14

The Water Molecule," *Theochem.*, 173-183 (1991).

PRESENTATIONS

1. Ab Initio Calculations of the Polarizabilities and Hyperpolarizabilities of Phosphaethyne. International Theoretical Chemistry Conference, University of Georgia, Athens, GA, October 1989.

2. Calculations on the Band Structure and Nonlinear Optical Properties of Organic Polymers. Oak Ridge National Laboratory, Oak Ridge, TN, September 1990.

3. Invited paper on "Theoretical calculations of interest to experimental spectroscopists" to be given at the XXth International Congress of Molecular Spectroscopy, August 27-30, Zagreb, Yugoslavia. Cancelled August 21 due to military action. Manuscript of talk to be published in *J. Mol. Structure*.

APPENDICES

I. Papers published (Not included; separately copyrighted)

II. Preliminary Manuscript, "Finite Field Ab Initio Calculations of the Dipole Polarizabilities and SEcond Hyperpolarizabilities II. Nitrogen Molecules," J. E. Bloor, P. C. Yih, and J. G. Yu.

III. Preliminary Manuscript, "Ab Initio Calculations of Polarizability of Quasi-One-Dimensional Polymers," J. G. Yu and J. E. Bloor.

IV. Preliminary Manuscript, "Theoretical Study on the Electronic Structure of Polyethylene, Polysiline and Polygermane," J. G. Yu and J. E. Bloor.

Appendix II

Finite Field Ab Initio Calculations of the
Dipole Polarizabilities and Second Hyperpolarizabilities II.
Nitrogen Molecules.

by

J. E. Bloor, P. C. Yih, and S. G. Yu
Department of Chemistry
University of Tennessee
Knoxville, TN 37996-1600

PRELIMINARY MANUSCRIPT

INTRODUCTION

There is currently a great interest in the design of organic materials with certain characteristic nonlinear optical properties. In order to understand the relationship between the electronic structure of molecules and their nonlinear properties a number of different semi empirical methods have been proposed. In order to place these methods on a sounder footing and also to extend their parameterization to elements for which very little experimental information is available we are systematically calculating accurate values of the dipole polarizabilities and the first and second hyperpolarizabilities for small molecules using the ab initio finite field method is implemented in the HONDO and the Gaussian computer codes. The calculations reported here are for a number of nitrogen compounds, namely ammonia, formamide, pyridine and pyrrole. For ammonia the results of very large basis sets are reported and compared to some recent similar calculations using slightly smaller basis sets. It is then shown that very similar results can also be obtained using smaller basis sets. The smaller basis sets are then used for the larger molecules and the results are compared with the results of semi empirical calculations.

RESULTS AND DISCUSSION

A.   Formamide

Formamide was chosen as an example of a medium sized molecule because there is widespread interest in the polarizabilities and hyperpolarizabilities of this molecule as a starting point for the development of parameters for the studies on intermolecular interactions of proteins and DNA. The molecule is also of interest as an example of the enhancement of nonlinear optical parameters due to charge transfer, i.e., between NH_2

as an electron donor and the carbonyl group as an electron acceptor.

The results of using different basis sets are reported in Table I. All calculations were performed at the HF 6-31G optimized geometry. The reference calculation I (column 2) was performed at the HF level with a 3-21G basis set supplemented on the C, O and N by one set of diffuse s, two sets of p and 3 sets of d polarization functions using the exponents suggested by Dykstra et al. A similar calculation was also performed in which a second diffuse p set (exp = 0.005) was included. As in the case of ammonia this omission had negligible effect and the results given in Table 1 are for a calculation which does not include this diffuse p function. The second p set was also omitted in the other calculations reported in Table 1..

Our ultimate aim is to perform calculations on larger molecules than formamide so the effect of replacing the core electrons by an effective core was investigated. These results are given in column 3 (Calc II). Except for the very sensitive β_{xzz} and β_{yzz} elements there was surprisingly little change but the computer time required was considerably reduced (by 30%). The ECP method was also used for Calc III and IV. In Calc III, Calc II was supplemented by two sets of p functions on the hydrogen. Although this addition doubled the computation time it had very little effect on the dipole polarizability tensor. There were however considerable changes in several of the β values, expecially the β_{xyy} term which was changed by 34%.

In Calc IV a d set (exp = 0.1) was added to the hydrogens. There was a negligible change in $\bar{\alpha}$ and only relatively small changes in the first and second hyperpolarizabilities, indicating that acceptable results can be obtained without going to

the expense of adding the d set. In Calc V a very small set of polarization functions, i.e., only one set each of d and p functions with exponents of 0.05 as suggested by DuPuis et al. for larger molecules was used. There was a loss in $\bar{\alpha}$ of only 11%, however, there were large changes in the β values showing that the results for the first hyperpolarizability using small basis sets could be unreliable. $\bar{\gamma}$ also changed by more than about 20%, indicating that first and second hyperpolarizabilities for polar molecules using a limited number of polarization functions may only have qualitative significance.

Finally, in order to assess the effort of including electron correlations the polarizability and first hyperpolarizability (HF and MP2) calculations were performed using the G90 computer code. The basis set was the standard 3-21G valence set supplemented by the polarization functions for carbon and nitrogen and hydrogen recommended by Dykstra (a total of 120 contracted functions). The results are summarized in Table 2. The HF calculation is very similar as expected to the ECP calculation III of Table 1. It can be seen that the effect of including electron correlation at the MP2 level is considerable on all the properties. The reduction of the dipole moment by 10.5% brings it into excellent agreement (3.71 Debyes). The average dipole polarizability is also increased by 12.7%, again bringing it into excellent agreement with an experimental value quoted by Waite et al. (*J. Chem. Phys.* 83, 4047 (1985). There are no experimental results for the hyperpolarizabilities with which to compare results for the β elements. This is unfortunate as the changes in these native elements including electron correlation are quite dramatic. However one must conclude that it is very important to either include electron correlation explicitly or to make a correction for it

before comparing with experiment.

B.   Pyridine

In order to assess the effect of destroying the symmetry of the benzene molecule on the nonlinear optical parameters, especially the β values which are course zero by symmetry in benzene, a number of calculations were performed on pyridine. These are compared with calculations on benzene in Table 3. Columns 2 and 3 are the results of a benzene (1β) and a pyridine (1P) calculation performed with the same basis set namely the standard 3-21G valence basis on the carbon, nitrogen and hydrogen supplemented by one set of p and one set of d functions on the carbon and nitrogens (a similar set has been used for recent literature calculations on benzene (*J. Phys. Chem.* **95**, 5873 (1991) and other enjinged hydrocarbons (*J. Phys. Chem.* **91**, 4728 (1989): *J. Chem. Phys.* **91**, 4728 (1989)). The results predict a small decrease in the average dipole polarizability largely due to a reduction in the out of plane matrix element and a drop in the average second hyperpolarizability ($\bar{\gamma}$) of about 20%. Column 4 contains the results (IIP) of adding a set of p functions (exp = 0.1) to the hydrogens. There is a small increase in the dipole polarizability and a further drop of 6% in the second hyperpolarizability. The first hyperpolarizabilities, as expected, are more sensitive, but even there the change in the most sensitive element β_{zzz} is only 13%. In column 5 are the results of a much larger calculation (IIIP) in which three sets of d polarization functions were used on the carbon and nitrogen using exponents taken from the triple zeta ELP set of Dykstra (i.e., 0.9, 0.13 and 0.02) and two sets of p polarization functions on the hydrogens. This made a total of 247 uncontracted Gaussian functions contracted to 207. This is close to the maximum

we can handle and consumed over three hours of CPU time on our IBM 3090/400 supercomputer to get the polarizabilities and first hyperpolarizabilities. (Since the G86 code was used for this calculation we were unable to get the second hyperpolarizabilities.) As expected, there are no dramatic changes in the results for the dipole polarizabilities but all three β elements were increased in magnitude with the largest change being in β_{zzz}, which was 40% larger than the result of Calc 1P. The results of all the calculations of the dipole polarizabilities are also in good agreement with the experimental values listed in column 7. This is in sharp contrast to the results of a recent semi empirical calculation (column 8). This calculation which is typical of most semi empirical calculations in the literature which almost universally tend to grossly underestimate the out of plane contributions to α because they do not contain the proper diffuse p and d functions. Since our calculations have shown that the diffuse function requirements for the calculation of β and γ values are even more demanding with respect to the number and type of functions added the semi empirical methods currently in use will yield very unreliable results for these parameters whereas even the small basis set we have used seems to give semi quantitatively correct results.

C.   Pyrrole

Pyrrole is a molecule of great interest with respect to its electronic properties because it is contained in many polymers with interesting semiconducting and nonlinear optical properties. There have been no previous ab initio calculations on the nonlinear optical properties. Our results using three different basis sets are summarized in Table 4. The results for $\bar{\alpha}$ and $\bar{\gamma}$ are very similar to those obtained for benzene. Certainly, there

is no enhancement shown by putting in the NH group instead of a carbon-carbon bond. The results show that there is little to be gained by including the p functions with exp = 0.9 on the hydrogens but that there is considerable change in the β values by using 1 set of p functions (exp = 0.1) on the hydrogens. This is unfortunate since their addition increases the size of the basis set by 1 function. Thus if values of β are needed (i.e., with an error less than 50%) a molecule the size of pyrrole is probably the limit that is practical at the present time, especially if as is important electron correlation is included.

CONCLUSIONS

The major conclusions of this work are that reasonable ab initio results, especially if an effective core potential (ECP) is employed, can be obtained for the dipole polarizabilities and the second hyperpolarizabilities of quite large molecules using a split valence (3-21G) basis set supplemented by two diffuse functions (d and p). On the other hand much larger sets are needed to get values of the second hyperpolarizabilities accurate to within fifty per cent even at the Hartree Fock level. The results on formamide also show that electron correlation is extremely important for the first hyperpolarizabilities, much greater than for the dipole polarizabilities. The results also show that current semi empirical methods are not even qualitatively correct especially for the out of plane contributions. (Note: In the final manuscript a table of comparison with results obtained using the new MOPAC semi empirical method will be included.)

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Table 1.   Nonlinear Parameters (α, β, γ) for Formamide.

	I[a]	II[b]	III[c]	IV[d]	V[e]
μ (Del)	4.207	4.194	4.190	4.169	4.55
α_{xx}	25.510	25.729	25.900	26.010	21.602
α_{xz}	2.806	2.930	2.954	2.983	2.033
α_{yy}	18.037	18.410	18.509	18.413	14.056
α_{zz}	28.55	28.798	28.980	29.090	29.080
$\bar{\alpha}$	24.033	24.311	24.463	24.505	21.588
$\Delta\alpha$					
β_{xxx}	39.605	41.404	41.633	45.310	60.792
β_{xxz}	17.507	18.800	19.633	21.035	28.310
β_{xyy}	5.536	7.404	9.908	9.088	12.720
β_{xzz}	7.949	8.071	7.646	7.666	8.762
β_{yyz}	17.777	15.821	14.827	15.103	20.783
β_{zzz}	-19.131	-18.913	-20.143	-19.750	-39.525
$\bar{\gamma}$	3175.86	3257.23	3343.98	3455.50	5514.68

[a]HF standard 32-1G set with 3D sets of polarization functions on C and N (Dykstra exponents), no pol functions on H (102 basis functions).

[b]ECP calculation same valence set as Calc I.

[c]ECP calculation as in Calc II but with 2 p pol. functions on H (exp = 0.9, 0.1).

[d]ECP calculation as in Calc III but with 1 d set added to H (exp = 0.1).

[e]ECP calculation using 1 p and 1 d set (exp = 0.05) on the C and N.

Table 2. MP2 Calculations on the Nonlinear Parameters of Formamide.

		HF[a]	MP2[a]
μ	μ(Deb)	4.190	3.750
	α_{xx}	25.870	28.928
	α_{xz}	2.88	3.456
	α_{yy}	18.190	20.033
	α_{zz}	28.852	33.195
	$\bar{\alpha}$	24.304	27.385
β	β_{xxx}	44.110	66.740
	β_{xxz}	20.687	23.170
	β_{xyy}	8.761	0.122
	β_{xzz}	7.426	12.179
	β_{yzz}	15.180	28.546
	β_{zzz}	-20.477	-16.476

[a]Standard 3-21G basis set supplemented by 2 p sets on H (exp = 0.9, 0.1 respectively)(120 basis functions).

Table 3. HFSCF Nonlinear Optical Parameters (α, β, γ) for Benzene and Pyridine.

	IB[a]	IP[a]	IIP[b]	IIIP[c]	IVP[d]	VP[e]	VIP[f]
μ	0.00	2.80	2.79	2.40			
α_{xx}	73.83	71.28	72.35	74.82	75.46	76.9	67.34
α_{yy}	73.83	66.097	67.07	69.55	70.07	70.2	59.85
α_{zz}	38.398	34.67	36.54	40.72	40.83	37.1	8.43
$\bar{\alpha}$	62.02	57.35	58.65	61.69	62.13	61.4	45.2
β_{xxy}	0.00	20.34	18.54	21.42	21.04		
β_{zzy}	0.00	16.80	16.90	21.32	18.16		
β_{yyy}	0.00	-10.347	8.98	-14.53	-10.40		
$\bar{\gamma}$	14,595.7	11,415.0	10,731				

[a]Basis set I: HF3-21G with 1 set of p and 1 set of d functions (exp = 0.050) on the carbon and nitrogen atoms.

[b]Basis set II: Basis set I and 1 set of p functions (exp = 0.1) on each hydrogen, total of 133 functions.

[c]Basis set III: HF3-21G with 1 diffuse s and 1 diffuse p and a 3d set on carbon and nitrogen as in the ELP set of Dykstra et al.

[d]Basis set IV: Basis set III supplemented by two sets of p functions on hydrogen (exp = 0.9, 0.1) as for the ELP set.

[e]Experimental results quoted in *Mol. Physics* 38, 577 (1979).

[f]Values are recent semi empirical values calculated using the MNDO method (*Theochem.* 236, 193 (1991).

Table 4.   Nonlinear Optical Parameters for Pyrrole.

	I[a]	II[b]	III[c]
μ (Deb)	1.917	1.858	1.867
α_{xx}	57.33	60.91	61.97
α_{yy}	33.606	38.44	39.00
α_{zz}	56.035	59.26	60.43
$\bar{\alpha}$	48.991	52.87	53.80
β_{xxz}	-28.88	-37.76	-40.244
β_{yyz}	17.310	33.58	34.704
β_{zzz}	20.99	35.101	36.33
γ_{xxxx}	21,322.58	18,260.97	
γ_{xxyy}	9,864.56	10,951.3	
γ_{xxzz}	4,257.78	3,331.2	
γ_{yyyy}	13,030.68	17,968.4	
γ_{yyzz}	5,859.08	5,722.7	
γ_{zzzz}	10,007.97	7,345.6	
$\bar{\gamma}$ (Av)	16,864.82	16,717.1	

[a]HF 3-21G with 1 set of p and 1 set of d polarization functions on C and N (exp = 0.05)(100 basis functions).

[b]HF as in Calc I but with 3 sets of d functions (exp = 0.9, 0.03, 0.02) on C and N and 1 set of p (exp = 0.1) on H using the ELP set of diffuse functions of Dykstra (180 basis functions).

[c]HF (G.86) as in [b] but with 2 sets of functions (exp = 0.9, 0.1) and 1 set of s functions (exp = 0.01) on H (200 basis functions).

Ab Initio Calculations of Polarizability of Quasi-One-Dimensional Polymers

Jianguo Yu and John E. Bloor

Department of Chemistry
The University of Tennessee
Knoxville, TN 37996-1600

and

J. Ladik
Chair for Theoretical Chemistry
of the Friedrich-Alexander-University
Erlangen-Nürnberg, D-8520 Erlangen, Eyerlandstr. 3, FRG

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ABSTRACT

The approach suggested by Ladik [6] for calculating polarizabilities of polymers is implemented to calculate the polarizabilities of polyethylene, polysilane and polygermane using a minimal basis set. The results using the same method of segmentation for all three polymers are in satisfactory agreement with accurate ab initio results for the corresponding oligomers.

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1. Introduction

Because polymers are now being recognized as having potential as a class of materials for electronics and optical applications, there has been considerable research in quite different scientific areas in an attempt to design polymers with the described properties. The design of polymers with suitable non-linear optical properties is one area which has recently been given a good deal of attention by both theoreticians and experimentalists.

In the dipole approximation, the microscopic response of a material to a uniform static electric field E can be described as

$$P_i(\vec{E}) = \mu_i + \sum_j \alpha_{ij}E_j + \sum_{jk} \beta_{ijk}E_jE_k + \sum_{jkl} \gamma_{ijkl}E_jE_kE_l + \ldots \qquad (1)$$

where μ_i is a component of the induced molecular dipole moment. α is the linear polarizability tensor and β and γ are quadratic and cubic hyperpolarizability tensors, respectively.

Within the one-electron restricted Hartree-Fock (RHF) approximation, two basically different approaches can be used to calculate the static (hyper)polarizabilities of molecules and oligomers: the finite-field (FF) and the sum-over-state (SOS) methods[1]. Basically, the SOS and FF methods correspond to different approximative levels of the perturbed Hartree-Fock theory. There have also been attempts to calculate (hyper)polarizability tensors on polyene oligomers as models for long chain polymers[2,3] using ab initio methods. These calculations however are very expensive and are limited

to the number of momomer units that can be utilized, e.g., 15 monomeric units in the case of polyenes[2].

Quite recently, Barbier et al[4] tried to use SOS scheme to calculate the polarizabilities of polymers directly. They adopted a perturbative method previously developed by Gerkin and Mednis[5]. In their calculations on a model molecular hydrogen chain and also on polyacetylene they used STO-3G basis set and found that the polarizability along the axis (α_{zz}) of the polymers were similar to those from calculations on the corresponding oligomers.

The FF approach formally equivalent to the coupled perturbed Hartree-Fock (CPHF) theory is basically superior to SOS method because it allows for the electrons to relax self-consistently in the presence of the perturbing electric field. There is however a fundamental difficulty, defined previously by Ladik in the IF approach. This is taht the addition of the external electric and one is not troubled by orbiting decisions on the type and number of excited states to include in the direction of the polymer chain destroys the periodic symmetry of the chain, which, unfortunately, is a requirement of the rigorous application of ab initio Hartree-Fock Crystal Orbital (CO) theory to polymers. Ladik[6] suggested an approximate method to solve the problem, in which the neighbor unit cells of the quasi-dimensional polymers were combined as segments and within each segment the values of the electric field are taken as a constant, but no applications were reported.

In the present paper, Ladik's method is implemented for the first time and tested by calculating the polarizability of some polymers.

2.   Theory

According to the ab initio SCF LCAO CO (Hartree-Fock) theory of periodic chains using Born-von Karman boundary conditions[7,8] for a linear polymer with z being the polymer axis, it is necessary to solve the following generalized matrix eigenvalue equation:

$$F(k) \, C_i(k) = \epsilon_i(k) \, S(k) \, C_i(k) \tag{2}$$

with

$$S(k) = \sum_{q=-N}^{N} e^{ikqa} S(q) \; ; \; [S(q)]_{rs} = \langle \chi_r^* | \chi_s^q \rangle \tag{3}$$

and

$$F(k) = \sum_{q=-N}^{N} e^{ikqa} F(q) \; ; \; [F(q)]_{rs} = \langle \chi_r^* | \hat{H}^N + \sum_{j=1}^{n^*} (2\hat{J}_j - \hat{K}_j) | \chi_s^q \rangle \tag{4}$$

In the presence of a homogenerous electric field E, the additional term $|e|rE$ will occur in $\hat{H}^N$ (eqn. (4)). The new Fock matrix is then

$$F(k,E) = \sum_{q=-N}^{N} e^{ikqa} F(q,E) \, , \; [F(q,E)]_{rs} = \langle \chi_r^* | \hat{H}^N + |e|rE + \sum_{j=1}^{n^*} (2\hat{J}_j - \hat{K}_j) | \chi_s^q \rangle = [F(q)]_{rs} + |e| \langle \chi_r^* | (rE | \chi_s^q \rangle \tag{5}$$

{XXXXXXXXXXXXXXXX}, Ladik[6] has proved that the supplemental term

$$\sum_{q=-N}^{N} e^{ikqa} \langle \chi_r^* | \; |e| \; rE \; |\chi_s^q \rangle \tag{6}$$

remains finite if a Gaussian basis is used despite the fact that $v = |e| \; rE$ is unbounded and the presence of **E** does not destroy the hermiticity of the Fock matrix:

$$F(\kappa, E)^+ = F(\kappa, E) \tag{7}$$

A more difficult problem introduced by the existance of $|e|rE$ is the aperiodicity caused by E_z. For an aperiodic chain, the whole formulas given by eqns (2) - (4) are no longer valid. Ladik suggested an approximate treatment for the aperiodicity to surmount the difficulty. The suggested procedure is to assume

$$|e|E_z \sum_{q=-N}^{N} e^{ikqa} \langle \chi_r^* |z| \chi_s^q \rangle = |e|E_z \langle \chi_r^* |z| \chi_s^* \rangle + \sum_{q=1}^{N} i2\sin(kqa) \; \langle \chi_r^* |z| \chi_s^q \rangle \tag{8}$$

for the case that E_z is not very large, instead of calculating the matrix elements $\langle \chi_r^\circ |E_z z| \chi_s^q \rangle$, it can be done dividing the chain of $2N + 1$ unit cells into $2\tilde{N} + 1$ segments ($\tilde{N} < N$) where each segment has a certain number of unit cells. In each segment m, z has an average value $\tilde{Z}_m$. If a constant number of cells is used for the segment length ℓ, then $2N + 1 = \ell(2\tilde{N} + 1)$ and eqn. (8) becomes

Therefore, in the presence of an electric field

$$|e|\overline{E}_z \sum_{q=-N}^{N} e^{ikqa} \langle \chi_r^* | z | \chi_s^q \rangle = |e|E_z \langle \chi_r^* | z | \chi_s^* \rangle + \sum_{q=1}^{N} 2i\sin(kqa) \langle \chi_r^* | z | \chi_s^q \rangle = |e|E_z [\tilde{Z}S_{rs}(0)$$

$$\sum_{q=1}^{N} 2i\sin(kqa) \frac{1}{N} \sum_{m=1}^{N} \tilde{Z}_m S_{r,s}(q)] \tag{9}$$

$$[F(k, E)_{rs} = \sum_{q=-N}^{N} e^{ikqa} \langle \chi_r^\circ | \hat{H}^N + \sum_{j=1}^{n^s} (2\hat{J}_j - \hat{K}_j) + |e|(E_x x + E_y y) | \chi_s^q \rangle +$$

$$|e|E_z [\tilde{Z}_1 S_{rs}(0) + \sum_{q=1}^{N} 2i \sin(kqa) \frac{1}{N} \sum_{m=1}^{N} \tilde{Z}_m S_{r,s}(q)] \tag{10}$$

The generalized eigenvalue equation is:

$$F_i(k, E) C_i(k, E) = C_i(k, E) S(k) C_i(k, E) \tag{11}$$

The one-electron wavefunctions in the presence of an electric field can be written as

$$\phi_i(k, rE) = \frac{1}{\sqrt{2N+1}} \sum_{q=-N}^{N} e^{ikqa} \sum_{q=1}^{m} c_{i,r}(k, E) \chi_r^q = \phi_I(E), I=i,k \tag{12}$$

where $\tilde{m}$ is the number of basis functions per unit cell. The dipole moment per unit cell induced by an electric field can be calculated as

$$\mu^{ind} = 2 \sum_I \langle \phi_I(E) | \hat{\mu} | \phi_I(E) \rangle = 2 \frac{a}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dk \sum_{i=1}^{n^x} \langle \phi_i(k, E) | er | \phi_i(k, E) \rangle \tag{13}$$

Sometimes, another definition of dipole moment can be given

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$$\mu^{ind} = \alpha E + 1/2\beta E^2 + 1/3!\gamma E^2 E + \ldots = \sum_{t=1}^{m} \frac{1}{t!}\alpha_t(E)^t \qquad (14)$$

Comparing above both equations, the tensor elements for the (hyper)polarizabilities can be calculated as

$$\alpha_{ij} = \frac{\partial \mu_i^{ind}}{\partial E_j}\Big|_{E=0} \qquad (15)$$

$$\beta_{ijk} = \frac{\partial^2 \mu_i^{ind}}{\partial E_j \partial E_k}\Big|_{E=0} \qquad (16)$$

$$\gamma_{ijkl} = \frac{\partial^3 \mu_i^{ind}}{\partial E_j \partial E_k \partial E_l}\Big|_{E=0} \qquad (17)$$

3. Computer Code

From the viewpoint of programing, in order to calculate polarizability and hyperpolarizability tensors of polymers, an additional one-electron intergral

$$\sum_{q=-N}^{N} e^{ikqa}\langle \chi_r^* || e |rE| \chi_s^q \rangle \qquad (18)$$

is added to original one-electron matrix. Eqn. (18) is the sum of dipole integrals $\langle \chi_i |\alpha| \chi_j \rangle - \alpha = x, y, \text{ or } z$ (19) weighted by the appropriate coefficients. The subroutines calculating dipole integrals

were supplied. With those integrals the first two additional integrals introduced by the presence of electrical field are obtained. The third term, which is the most important for the study of non linear optical properties of polymer, is more difficult to calculate. It is necessary to choose the parameters $\tilde{Z}_1$, $\tilde{Z}_m$ and $\bar{N}$, followed by the summation over overlap integrals given in eqn. (10).

With newly joined Fock matrix F(k, E) and solving the eigenvalue equation in the presence of electrical field (eqn. (11)),

$$F_i(k, E) C_i(k, E) = C_i(k, E) S(k) C_i(k, E) \tag{11}$$

Sometimes, with the help of dipole integrals, the induced dipole moment μ^{ind} can be easily calculated.

Numerical differentiation is then applied to get polarization and hyperpolarization tensors. The usually used value for the components of the electric field is 0.001 a.u. For example, with E_z of 0.001 a.u. α_{zz} can be calculated as

$$\alpha_{zz} = \frac{[\mu_z^{ind}(E_z) - \mu_z^{ind}(-E_z)]}{2E_z} \tag{20}$$

The calculation of α_{xx} and α_{yy} can be calculated in the usual way.

4.   Results

(a) α_{zz} and α_{yy}

Table 1 shows comparative results of α_{xx} and α_{yy} calculated with the polymer

program with HONDO calculations for some general long-chain oligomers.

The results of the two methods for all three systems (polyethelene, polysilane and polygermane) are in very good agreement. However, its results of polymer calculations are all smaller than the HONDO calculations. The α_{xx} and α_{yy} values are for the $H(C_2H_4)_nH$ unit in the two molecules, n equals 5 or 7. Because we are calculating for the infinite linear polymer it is reasonable to assume that the longer the model molecule used the more precise the result obtained. The values of the α_{xx} and α_{yy} in $H(C_2H_4)_7H$ calculation are less than those of $H(C_2H_4)_5H$ and the results on the polymer have negative errors compared to those of $H(C_2H_4)_5H$. We conclude from this that the approach taken does produce satisfactory results for the calculation of α_{xx} and α_{yy} for polymers.

(b) The choice of parameters in calculation of α_{zz}

A much more difficult problem is the calculation of α_{zz}, the polarizability along the axis polymer chain. The difficulty is that the presence of electric field this direction destroys the periodicity of the polymers which results in problems in solving the resulting Fock equations. Ladik's approximation has solved the problem. In implementing the method proposed by Ladik it is necessary to choose the parameters $\check{Z}$, $\check{Z}_m$ and $\tilde{N}$ (m > 1), i.e., we have to decide how to divide into segments and how to choose the average electric field in each segment. We have been unable to arrive at a theoretical background for choice, so that we have had to resort to this trial and error. There have been no previous attempts to solve this problem in practice.

Our first example is polyethylene. The contribution for α_{zz} of both diagonal blocks

of electric field integral $<\chi_i° \, | \, |e| E_z | \chi_i°>$ and non-diagonal blocks $<\chi_r° \, | \, |e| E_z | \chi_s^q>$

have been analyzed and it was found that according to Ladik's approximation

$$<\chi_r^* ||e|E_z z|\chi_s^*> \approx |e|E_z \tilde{Z}_1 S_{rs}(0)$$

and that the contribution of above term for α_{zz} is zero. In the present approahc then use

of $\tilde{Z}_1(-1)^n Srs(0)$ instead of $<\chi_r°|e|E z|\chi_s°>$ when N is even then $<\chi_r°|z|\chi_s°> \geq 0$, and

when N is odd then $<\chi_r° \, |z| \, \chi_s°> \, < 0$, i.e., the sign of the integral is chosen through N.

Table 3 presents the contributions of the diagonal and non-diagonal blocks for α_{zz}

for polyethylene using a STO-3G basis set. In these calculations we used 1.25 as $\tilde{Z}_1$,

which is an approximately a quarter of the translation vector length. These results show

that the dominant contribution to α_{zz} is from the diagonal blocks while the non-diagonal

blocks' contribution is less important. In these above calculations three neighbor units

were taken as a segment and the choice $\tilde{Z}_m = m\tilde{Z}_1$ was used. Because non-diagonal

blocks are less important the results of changing the method of dividing the segments

have no remarkable effect. In the calculations on the other polymers, we adopt the same

choice as for polyethylene for the needed parameters.

5. Polarizabilities of polysilane and polygermane

The calculations for polyethylene showed that a quarter of the translation vector

length α_0 is a suitable value for $\tilde{Z}_1$. Using this choice and the same choice for $\tilde{Z}_1$, $\tilde{Z}m$

and $\bar{N}$, α_{zz} of polysilyane and polygermane were calculated. The suitable values of $\tilde{Z}$ for

polysilicane and polygermane is $1.25 \times 1/4 \times \alpha_0$. The results agree well with the accurate

calculations on the oligomers.

CONCLUSIONS

The results are the first attempt to calculate the polarizabilities of an infinite chain polymer. The results for polyethylene, polysiline, and polygermane seem reasonable. They show the enormous increas in the α_{zz} expected as carbon is replaced by silicon and then by germanium.

Attempts are in progress to extend this approach to other polymers and to use a more realistic basis set.

ACKNOWLEDGEMENTS

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Table 1.　Comparison of electric polarizabilities α_{xx} and α_{yy}. All of the calculations were done with STO-3G basis set. For HONDO calculations the oligomers $H(X_2H_4)_5H$, $X = C$, Si, and Ge were adopted and for polymer calculations, the number of neighbors was taken as five.

System	C_2H_4			Si_2H_4			Ge_2H_4		
	Oligomer	Polymer	Difference %	Oligomer	Polymer	Difference %	Oligomer	Polymer	Difference %
α_{xx}	10.039	9.709	-3.4	19.920	19.536	-1.9	25.023	24.243	-3.1
α_{yy}	9.804	9.368	-4.4	23.648	23.145	-2.1	34.388	33.220	-3.4

Table 2. The effect of different number of neighbors in calculations of α_{xx} and α_{yy} for polyethylene oligomers.

	H-$(C_2H_4)_5$-H	H-$(C_2H_4)_7$-H
α_{xx}	10.039	9.941
α_{yy}	9.804	9.690

Table 3.   The contributions of diagonal and non-diagonal segments to α_{zz} in the calculation of polyethylene.

Number of Neighbors	only diagonal	only non-diagonal
1	-11.316	1.121
2	-12.571	1.115
3	-12.989	1.122
4	-13.182	1.124
5	-13.285	1.125
6	-13.347	1.125
7	-13.387	1.125
8	-13.414	1.125
9	-13.417	1.132

Table 4.   Comparison of polarizabilities of polyethylene, polysilane and
            polygermane with polymers and oligomers calculation.

	C_2H_4		Si_2H_4		Ge_2H_4	
	Oligomer	Polymer	Oligomer	Polymer	Oligomer	Polymer
α_{xx}	10.039	9.709	19.920	19.536	25.023	24.243
α_{yy}	9.804	9.368	23.648	23.145	34.388	33.220
$\alpha_{\varsigma\varsigma}$	12.829	12.164	46.298	45.825	109.747	112.230

THEORETICAL STUDY ON THE ELECTRONIC STRUCTURE OF POLYETHYLENE, POLYSILANE AND POLYGERMANE

by

Jianguo Yu and John E. Bloor

Department of Chemistry
The University of Tennessee
Knoxville, TN 37996-1600

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Abstract

The electrical structures of polyethylene, polysilane and polygermane have been calculated by the ab initio SCFCO method using a number of different basis sets. The band gaps, band widths, ionization potentials, electron affinities and density of states (DOS) of the polymers are compared. The effects of different basis sets and different numbers of interacting neighbors on the energy band figures using electrical structures of the polymers are discussed. The conduction mechanism of polysilane and polygermane is explored using energy band figures.

I. Introduction

There is a very great interest in the semiconducting properties of polysilanes and polygermanes in recent years because of the potential technological applications of these materials. The understanding of these properties requires information on their electronic structure - especially the band-edge electronic structure and the conduction band. While for the electrical structures of polyethylenes and polysilanes there have been previous theoretical studies, both at the semi empirical [1-4] and ab initio [5-10] level, there has been for polygermane only the work by Takada et. al. [1] using the first principle local density functional method.

In this paper, the ab initio RHFCO method developed by Ladik's group [] is used in the comparative study of electrical structure and conduction properties of polyethylene, polysilane and polygermane. The important electronic properties such as band gap and band widths, ionization potential, electron affinity and density of states (DOS) of those polymers are compared. The effects of including 3d orbitals in the calculations on polysilane is discussed and the influence of substituting methyl groups into polysilane is investigated. The conduction mechanism of polysilane and polygermane is also explored.

II. Methods and Computational Details

The energy band structures of the one-dimensional periodic neutral polymers were calculated using the ab initio Hartree-Fock crystal orbital method [12]. To obtain information on how the electronic and energetic properties of the macromolecules depend on the choice of the basis set the minimal STO-3G [13], 3-21G [14], 6-31G [15] and Clementi's double-zeta [16] basis sets were used. In some calculations on Si these basis sets were supplemented by d polarization functions.

For all the three polymers the planar zigzag structure (figure 1) was adopted.

The geometrical parameters of the polymers used in the calculations are given in Table 1. The geometrical parameters of polyethylene are taken from Otto et. al. [17]. The optimized values for the geometry of polysilane obtained from molecular mechanics calculations was adopted [18]. For polygermane the optimized values from ab initio 3-21G calculations for oligomers of $H(Ge_2H_4)_nH$ (n -) were used to construct the geometry of the polymer unit cells [19].

The effect of methyl substitution for silicon polymer was studied by comparing the electronic structure of polysilane and poly(dimethylsilyne) with different basis sets. The geometry of polydimethylsilyne is based on the molecular mechanics optimization of reference 18.

All calculations were performed on an IBM 3090/200 computer at the University of Tennessee Computing Center (UTCC) using the ab initio polymer program POLYMER from (   ).

III. Results and Discussion

1.   The effect of the different number of interaction neighbors.

In Table 2 the theoretical results for polyethylene and polysilane in terms of different number of interacting neighbors with both STO-3G and

Clementi's basis sets are reported. These results show that as the number of neighbors is increased for both polymers (polyethylene and polysilane) and with the difference basis sets for polyethylene, the valence and conductive band gaps are shifted toward higher energy. However the changes in the width of these bands is negligible. The changes in the ionization potentials and electron affinity with different numbers of interaction neighbors have the same trends, i.e., the ionization potentials become smaller and the electron affinities get bigger. The calculations show that whereas there is a considerable change in the band gaps in increasing the number of nearest neighbors from 2 to 5 for both polymers and for both basis sets for polyethylene it is the further increase from five to eight cause little further change.

2.   The effects of basis sets on electronic band structure.

Table 3 presents the electrical structure of polyethylene, polysilane and polygermane with different basis sets.

For polyethylene, the results with STO-3G and Clementi's basis sets show big differences. The valence band shift to lower energy about 1 eV and its width becomes narrower. The change in the conduction band is more marked. It is lowered by about 11 eV which changes the band gap of the polymer from 23.97 eV for STO-3G to 14.60 eV for Clementi's basis set. Most of this change is in the electron affinity which changes from 14.07 eV to 3.29 eV.

For polysilane, the same trend as polyethylene is exhibited. In polysilane, the shift of valence band is more remarkable (from STO-3G to 6-31G it shifts toward lower energy about 2.2 eV, with Clementi's basis set, the band further shifts about 2.6 eV toward lower energy). The conductive band move about 9 eV toward lower energy from STO-3G to

Clementi's basis sets and the width of the band becomes only 1.6 eV from 3.7 eV of STO-3G. The more noticeable result is that the minimum of conductive band with Clementi's basis set becomes negative, which makes the electron affinity have a negative value. The change of the band gap of the polymer from STO-3G to Clementi's basis set isn't as big as polyethylene which change from 14.1 to 10.2 eV.

Because of convergence difficulties with the large basis sets only STO-3G and 3-21G calculations can be reported for polygermane. The same trend of the electronic structure change from minimum STO-3G to double-zeta valence 3-21G can be seen, which with the valence 3-21G, the conductive bands shift toward lower energy. Because the basis sets only have little difference the change of electrical structure of polygermane isn't as distinct as both polyethylene and polysilane.

3. The effect of 3d functions in the calculation of electronic structure of polysilane and poly(dimethylsilylene).

For the system including Si atoms, the effect of 3d functions still is a negligibleless problem. For polysilane and poly(dimethylsilylene), the energy band structures were calculated with STO-3G and STO-3G* (a set of 3d functions of Si atom with exponent = 0.39 was supplied to STO-3G basis set) and the results are presented in Table 4. These results show that the addition of 3d function on the Si atoms produces little effect on the band structure of both polysilane and poly(dimethylsilylene) and the effect is like that using bigger basis sets shown in last section. This shows that the 3d functions aren't necessary for a qualitative comparative study of band structure of polysilane and substituted silicon polymers.

4. The comparison of polysilane and poly(dimethylsilylene).

The substitution of methyl groups into polysilane shifts both the

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valence and conductive bands about 1 eV toward higher energy, and the widths of valence bands become 1 eV narrower while the conduction band becomes 1.5 eV wider. The band gap is about 1 eV narrower in poly(dimethylsilylene) than in polysilane.

5.   A comparison of conduction properties of polyethylene, polysilane and polygermane.

In Table 3 are listed the band gaps of polyethylene, polysilane and polygermane. The experimental value of band-gap of polyethylene is 8.8 eV [20]. With 6-31G** basis set and both RHF and MP methods, Sahai [11] obtained 13.4 and 10.3 eV for the band-gap of polyethylene respectively. Our result with Clementi's basis set is very similar Sahai's RHF value. It's well-know that RHF method overestimate the band-gap. In our calculation for polysilane with Clementi's basis set the band-gap is 10.2 eV. Using same basis set and RHF CO method for polyethylene, calculated band-gap is about 6 eV larger than experimental that. According to this proportion, the band-gap should be about 4.2 eV, which is approach that gotten by other ab initio and semi empirical researchers [1-10].

For polygermane only STO-3G and 3-21G basis sets were used. The band gaps gotten with both the basis sets are 9.3 and 9.5 eV respectively. In terms of STO-3G basis set, the band-gap of polygermane is 4.3 eV smaller than that of polysilane. It can be expected that polygermane would have much smaller band gap than polysilane. In the local density functional calculation [10] by Takada et. al. the difference between the band gaps of polysilane and polygermane is only 0.6 eV.

Despite this contradiction we can still draw the conclusion that polysilane and polygermane have a much more smaller band gap than polyethylene, although the atoms C, Si and Ge of those polymers are in

same group in the periodic table. The difference is the essential property which makes polysilane and polygermane semiconductors and polyethylene a typical insulator.

Figure 1 presents the energy-band structures of polyethylene, polysilane and polygermane with STO-3G calculations. This figure shows that beside the difference in band-gaps there is also a difference in energy band profiles.

For each polymer the first six highest occupied valence bands (HOVB) and the first four lowest unoccupied conduction bands (LUCB) are drawn. Solid and broken lines indicate σ bands and π bands, respectively. The HOVB's of all three polymers are σ orbitals, consisting of positive overlap between the Pz orbitals, the difference between polyethylene and the other two polymers, polysilane and polygermane, is that the energy bands of polysilane and polygermane are highest occupied throughout, while in the majority of K, the highest occupied valence band of polyethylene is a π band which consists of σ the negative overlaps between Pz orbital of both carbon atoms and between Px orbitals of each carbon atom and 1s orbital of neighboring H atoms. Nelson and Pietro [21] have previously pointed out that polysilanes conduct through extensive σ delocalization and we have also found that [19] the polygermanes are very similar. Besides having bigger band gap, the energy band crossing can be thought as a reason polyethylene is an insulator.

From an analysis of the coefficients of the band orbitals it can be found that the LUCB of polyethylene are different in composition to those of both polysilane and polygermane. The LUCB's of the latter two consist of negative overlap of SP hybridized orbitals of the Si or Ge atoms, while those of polyethylene have a contribution from the H orbitals besides SP

overlap.

On the profile, as its valence band, the LUCB of polyethylene crosses with π^* crystal bands while those of polysilane and polygermane do not. All of above those can be explained as the reason that polysilane and polygermane are semi conductors while polyethylene is a insulator.

6. Density of states.

The density of electronic states (DOS) for polyethylene, polysilane and polygermane are shown in Figure 2. The calculation of the DOS only included first six HOVB's and first four LUVB's for each polymer. The results computed with the help of the STO-3G minimal basis set have been used for the graphics. It can be seen from the comparison oᴸ the DOS of valence band that those of polysilane and polygermane have similar shape, although the position of peaks of polygermane is about 2 eV lower than those of polysilane. The shape of DOS of polyethylene is different with those of polysilane and polygermane. The DOS of conduction bands of polyethylene is more concentrated, while the DOS of conduction bands of polysilane has a maximum about 12 Ev. In the figure of the DOS of conduction bands of polygermane four peaks can be distinguished, corresponding with four conduction bands.

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Table 1. The Geometrical Parameters (Distances in Å and angles in degree)

System poly-	R_{X-X}	R_{X-H}	<XXX	<HXH		
(C_2H_4)	1.54	1.09	109.5	109.5		
(Si_2H_4)	2.34	1.48	109.4	107.4		
(Ge_2H_4)	2.47	1.53	112.0	109.0		
		R_{Si-C}	R_{C-H}	<HCH	<SiSiC	<SiCH
($Si_2(CH_3)_4$)	2.35	1.87	1.10	115.4	108.5	110.0

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Table 2. The effect of number of neighbors (units = eV)

System poly-	basis set	Number of neighbors	Valence band			Conduction band			Gap	Ionization potential	Electron affinity
			Emin	Emax	width	Emin	Emax	width			
(CH₂)	STO-3G	2	-14.2489	-9.8946	4.3543	14.0741	19.4323	5.3582	23.9687	9.9846	14.0741
(CH₂)	STO-3G	5	-13.7677	-9.3963	4.3714	14.7439	19.9654	5.2215	24.1402	9.3963	14.7439
(CH₂)	STO-3G	8	-13.6173	-9.2259	4.3914	14.8790	20.1198	5.2408	24.1048	9.2259	14.8790
(CH₂)	Clementi's	2	-15.2810	-11.3050	3.9760	3.2945	7.5932	4.2987	14.5995	11.3050	3.2845
(CH₂)	Clementi's	5	-14.7241	-10.7685	3.9556	4.0113	8.3328	4.3214	14.7799	10.7685	4.0113
(SiH₂)	STO-3G	2	-10.5011	-6.4082	4.0929	7.6693	11.3506	3.6812	14.0775	6.4082	7.6693
(SiH₂)	STO-3G	5	-10.0852	-6.0204	4.0648	8.1630	11.7499	3.5869	14.1834	6.0204	8.1630
(SiH₂)	STO-3G	8	-9.9624	-5.8869	4.0755	8.2629	11.8700	3.6071	14.1498	5.8869	8.2629

Table 3. The band characteristics of polyethylene, polysilane and polygermane using different basis sets (all energy values in eV)

System poly-	Basis Set	Valence band			Conduction band			Gap	Ionization potential	Electron affinity
		Emin	Emax	width	Emin	Emax	width			
(CH_2)	STO-3G	-14.2489	-9.8946	4.3543	14.0741	14.4323	5.3582	23.9687	9.9846	14.0741
(CH_2)	Clementi's	-15.2810	-11.3050	3.9760	3.2945	7.5932	4.2987	14.5995	11.3050	3.2945
(SiH_4)	STO-3G	-10.5008	-6.4049	4.0959	7.6656	11.3506	3.6850	14.0705	6.4049	7.6656
(SiH_4)	6-31G	-12.7265	-9.0173	3.7091	2.9421	6.0556	3.1134	11.9595	9.0173	2.9421
(SiH_4)	Clementi's	-15.4184	-11.5491	3.8693	-1.3020	0.3050	1.6070	10.2471	11.5491	-1.3020
(GeH_2)	STO-3G	-12.3745	-9.1298	3.2447	0.1674	4.8575	4.6901	9.2973	9.1298	0.1674
(GeH_2)	3-21G	-11.6527	-8.1803	3.4724	1.2756	3.1953	1.9197	9.4560	8.1803	1.2756

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Table 4. The electrical structures of polysilane and poly(dimethylsilylene) with STO-3G and STO-3G* basis sets (number of neighbors is two, energies are in eV)

Polymers	Basis sets	Valence band			Conduction band			Gap	Ionization potential	Electron affinity
		Emin	Emax	width	Emin	Emax	width			
polysilane	STO-3G	-10.5008	-6.4049	4.0959	7.6656	11.3506	3.6850	14.075	6.4049	7.6656
	STO-3G*	-10.5908	-6.9036	3.6871	6.4120	10.0795	3.6676	13.3156	6.9036	6.4120
poly(dimethyl-silylene)	STO-3G	-9.4285	-6.3983	3.0303	6.4903	11.6763	5.1860	12.8886	6.3983	6.4903
	STO-3G*	-9.4770	-6.8249	2.6521	5.8367	10.4154	4.5788	12.6616	6.8249	5.8367

Figure Captions

Figure 1. Band structure of (a) Polyethylene, (b) Polysilane and (c) Polygermane.

Figure 2. Density of states (DOS) of (a) the valence band and (b) the conduction band of polygermane, (c) the valence band and (d) the conduction of polysilane and (e) the valence band and (f) the conduction band of polygermane. The horizontal axis is energy in eV.